Aqueous–gas phase partitioning and hydrolysis of organic iodides

G.A. Glowa and J.C. Wren

Abstract: The volatility and decomposition of organic iodides in a reactor containment building are important parameters to consider when assessing the potential consequences of a nuclear reactor accident. However, there are few experimental data available for the volatilities (often reported as partition coefficients) or few rate constants regarding the decomposition (via hydrolysis) of organic iodides. The partition coefficients and hydrolysis rate constants of eight organic iodides, having a range of molecular structures, have been measured in the current studies. This data, and data accumulated in the literature, have been reviewed and discussed to provide guidelines for appropriate organization of organic iodides for the purpose of modelling iodine behaviour under postulated nuclear reactor accident conditions. After assessment of the partition coefficients and their temperature dependences of many classes of organic compounds, it was found that organic iodides could be divided into two categories based upon their volatility relative to molecular iodine. Similarly, hydrolysis rates and their temperature dependences are assigned to the two categories of organic iodides.

Key words: organic iodide, hydrolysis, partition coefficient, iodine behaviour model, nuclear reactor safety.

Résumé : La volatilité et la décomposition d'iodures organiques dans un bâtiment contenant un réacteur sont des paramètres importants à considérer lorsqu'on évalue les conséquences potentielles d'un accident à un réacteur nucléaire. Toutefois, il y a peu de données expérimentales relatives aux volatilités (souvent rapportées sous la forme de coefficient de partage) ou de constantes de vitesse concernant la décomposition (par voie d'hydrolyse) des iodures organiques. Dans le présent travail, on a mesuré les coefficients de partage et les constantes d'hydrolyse de huit iodures organiques représentatifs de diverses structures moléculaires. On a fait une revue de ces données et de celles recueillies dans la littérature et on en discute dans le but de fournir des indications claires pour l'organisation appropriée des iodures organiques dans le but d'établir un modèle du comportement de l'iode dans les conditions postulées lors d'un accident dans un réacteur nucléaire. Après une évaluation des coefficients de partage de plusieurs classes de composés organiques et de leurs dépendances sur la température, on a trouvé que les composés organiques peuvent être divisés en deux catégories suivant leur volatilité relative en iode organique. Les vitesses d'hydrolyse et leurs dépendances sur la température ont aussi été divisées de la même manière.

Mots clés : iodure organique, hydrolyse, coefficient de partage, modèle de comportement de l'iode, sécurité d'un réacteur nucléaire.

[Traduit par la Rédaction]

1. Introduction

The production and decomposition of volatile forms of radioiodine in, and their release from, a reactor containment building are important processes to consider when assessing the potential consequences of a nuclear reactor accident. A considerable number of studies on these processes have been carried out with the objective of developing a model that can predict iodine volatility in containment during the course of an accident (1–6). Recent critical reviews on iodine behaviour in containment (7, 8, and refs. therein) provide a comprehensive technical background on this subject.

Iodine would be released into the containment atmosphere from fuel via the reactor coolant system, mainly as nonvolatile species (e.g., CsI under most accident conditions) (8). The initial fraction of volatile iodine species (i.e., molecular iodine and organic iodides) in containment would be very small. However, although CsI is water soluble and would initially be dissolved in containment water, a small fraction of the nonvolatile I^- initially dissolved in water would be continuously oxidized to volatile molecular iodine (I_2) in the presence of the high radiation field following an accident. Molecular iodine reacts easily with organic compounds in the presence of radiation to form organic iodides. Therefore, a significant portion of the gaseous iodine in containment would be in the form of organic iodides. Measurements at the TMI (Three Mile Island) 2-reactor following the 1979 accident showed that organic iodides were a major component of the small amount of iodine that became airborne (9). Studies on total iodine volatility under containment accident

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conditions in an intermediate-scale facility have also shown that the organic iodide fraction in the gas phase could be as high as 90% in the presence of painted surfaces (7). Organic iodides are thus very important in the assessment of the radiological consequences of a nuclear reactor accident.

Early studies on organic iodide formation and decomposition under potential nuclear reactor accident conditions focused mainly on CH_3I because it is the simplest organic iodide with a high volatility. Recent studies have shown, however, that organic iodides are formed mainly from the reaction of I_2 with organic impurities in the aqueous phase, which then become airborne, and that a large fraction of the organic iodides formed in the aqueous phase under containment conditions would be less volatile than CH_3I (7, 10, 11). A wide range of organic radicals may be formed by the radiolytic degradation (10) of a wide range of organic impurities dissolved in the containment sump water from containment paints (7, 11). This, in turn, leads to formation of a wide range of organic iodides, whose volatility and decomposition rates differ considerably. The contribution of each of these species to the overall iodine gas-phase concentration will therefore vary considerably from one species to another. Therefore, the partition coefficients and hydrolysis rate constants of eight organic iodides, having a range of molecular structures, have been measured in the current studies.

2. Background

Although the possibility of formation of various organic iodides in containment had been recognized, early studies on organic iodide formation focused mainly on CH_3I. As mentioned above, this was because it is the simplest organic iodide, and it has a high volatility. Radioiodine Test Facility (RTF)[2] experiments performed in painted vessels have found, however, that a large fraction of the organic iodides formed from containment paint impurities are less volatile than CH_3I (7). Formation of low volatility compounds has been further supported by bench-scale studies on the dissolution of organic solvents from painted surfaces into water (11, 12) and on the radiolytic decomposition of organic impurities in water (10, 13–18). Studies on the dissolution of organic solvents from painted surfaces have shown that the molecular structure of compounds released varies (e.g., aromatics, alcohols, and ketones), and that commonly used paint solvents contain from one to 10 carbons (Table 1). Calculations suggest that the amount of organic solvents released from painted surfaces into the sump could result in concentrations of up to 1×10^{-2} mol dm^{-3} (11, 12). (Note that this concentration is subject to many parameters that would be accident scenario and reactor specific such as paint thickness, paint age, compound solubility, water volume, and paint area in contact with water, etc.).

Table 1. Some commonly used paint solvents.

No. of carbons	Organic solvent constituents
1	Methanol
2	Ethanol
3	Propanol, propanone
4	2-Butanone, butanol
5	Furfuryl alcohol
6	4-Methyl-2-pentanone
7	2-Heptanone, methylbenzene
8	Xylene, ethylbenzene
9	Trimethyl benzene

Once released into the sump water, these organic solvents would undergo radiolytic decomposition. Studies on methyl ethyl ketone (MEK) in the absence of iodine species (10,13,14) have shown that the radiolytic decomposition of MEK in the aqueous phase under aerated conditions results in the sequential formation of smaller and more oxidized organic compounds, and eventually complete conversion to CO_2:

$$[1] \qquad RH(aq) + \cdot OH(aq) \rightarrow R\cdot(aq) + H_2O$$

$$[2] \qquad R\cdot(aq) + O_2(aq) \rightarrow RO_2\cdot(aq) \rightarrow\rightarrow R'\cdot, \text{ alcohols, aldehydes, acids, and } CO_2$$

where RH and R· (or R′·) represent an organic compound and organic radical, respectively. Among the intermediate decomposition products observed during the radiolysis of MEK were 3-hydroxy-2-butanone, 2,3-butanedione, ethanoic acid, ethanal, and methanal (13).

The dissolution and MEK radiolysis studies imply that the range of organic compounds present in the sump could be considerable, with a large proportion of them being highly soluble oxygen-containing compounds (i.e., alcohols, ketones, and carboxylic acids). Various organic radicals would be formed from these organic compounds and, in the presence of I_2, which is known as a very good radical scavenger, a small fraction of the radicals would react with I_2 to form organic iodides:

$$[3] \qquad R\cdot(aq) \text{ (or } R'\cdot(aq)) + I_2(aq) \rightarrow RI(aq) \text{ (or } R'I) + I(aq)$$

where RI (or R′I) represents an organic iodide. Consequently, the range of organic iodides formed under containment accident conditions could be large and could include alkyl iodides, iodoketones, -alcohols, -phenols, and -acids. With the exception of the alkyl iodides, these species would have low volatility (discussed in Section 5.2), and would be very difficult to detect in the gas phase. Generally, only alkyl iodides are detected during RTF tests, or bench-scale experiments (15) by gas chromatographic methods.

Organic iodides, which can be formed in irradiated solutions of iodide and organic compounds (7, 15, 16), will partition between the aqueous and gas phases (rxn. [4]) according to Henry's Law (see Section 3.2). Meanwhile, organic iodides in the aqueous phase will undergo decomposition via hydrolysis (rxn. [5]) and radiolysis (rxn. [6]).

$$[4] \qquad RI(aq) \leftrightarrow RI(g)$$

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[2] The Radioiodine Test Facility (RTF) is an intermediate scale facility containing a 345 dm^3 containment vessel that provides a combination of potential reaction media (gas phase, aqueous phase, and a variety of surfaces) and conditions (pH, temperature, radiation, initial concentrations, and speciation of iodine), to simulate a reactor containment building following an accident (7).

[5] $RI(aq) + H_2O \rightarrow ROH(aq) + I^- + H^+$

[6] $RI(aq) + e^-_{aq} \rightarrow R\cdot(aq) + I^-$

Therefore, to determine the overall behaviour of organic iodides, and their contributions to the gaseous iodine concentration under containment accident conditions, the formation and the decomposition of organic iodides must be adequately quantified. The rate of the hydrated electron reaction (rxn. [6]) is diffusion-controlled and is therefore nearly independent of the type of organic iodide. Therefore, the current study focuses on the partitioning and the hydrolysis of organic iodides. The partition coefficients (see Section 3.2 for its definition) and the hydrolysis rate constants of a range of organic iodides have been measured, and compared with the literature data of organic iodides, if available, and also with compounds of similar structure that do not contain iodine. These values were reviewed for the purpose of providing guidelines to appropriately group organic iodides so that modelling of organic iodide behaviour under radiolytic conditions can be more easily managed.

3. Experimental

A small set of compounds was chosen to cover the major structural possibilities (methyl, primary, secondary, tertiary, benzyl, aryl) of organic compounds that may be present in reactor containment. For example, a primary alcohol (iodoethanol) and a carboxylic acid (iodoethanoic acid) were chosen to explore the effect of neighbouring oxygen-containing functional groups on hydrolysis rate and partition coefficients. All compounds studied were purchased from Aldrich Chemical Co., except (iodomethyl)benzene, which was from Alfa-Aesar (a Johnson Matthey company), and 2-iodobenzenol, which was from ICN Biomedicals Inc. Compounds were of the highest purity available and were used as received without further purification.

3.1 Measurement of hydrolysis rates

Two methods were used to study the hydrolysis rates of these compounds. The first method used a solid-state ion selective electrode (ISE) designed for iodide measurements (Orion 9553) with a double junction reference electrode (Orion 900200) to measure the concentration of iodide produced by hydrolysis. These probes were connected to a Fisher Accumet 950 pH meter. The electrode was calibrated for each temperature of interest using NaI solutions of known concentration. The plot of mV vs. $\log_{10}$ [I^-] was found to be linear over the concentration range studied. This method was successfully used for the hydrolysis of 2-iodobutane. Due to baseline drift however, this method was found to be unsuitable for the time periods required to measure the hydrolysis rates of the other compounds.

For the majority of the studies, the hydrolysis rates were determined from the growth of the absorbance of I^- (ε = 12 980 $dm^3\ mol^{-1}\ cm^{-1}$ at 225 nm) monitored using a HP 8450A spectrometer. In some cases there was minor absorbance at 225 nm attributed to the starting material and (or) the resulting alcohol, in addition to the absorbance by I^-. But because the change in concentration of the three components (organic iodide, alcohol, and I^-) occurs at the same rate, the first-order hydrolysis rate constant of the organic compound can still be obtained from the change in absorbance at 225 nm (see Section 4.1 for the relationship between the absorbance and the first-order rate constant).

In general, the measurements were repeated at least once. The reproducibility of the measurements was better (<5%) when measuring fast hydrolysis rates (i.e., for 2-iodobutane and (iodomethyl)benzene). During the measurement of slow hydrolysis rates (i.e., iodomethane and iodoethane), reproducibility was generally in the 20% range. Measurements lasted between 3–5 half-lives during experiments using the electrode method. For each spectrometer measurement, the absorbance at 225 nm was then monitored until a limiting absorbance was approached (generally > 3 half-lives).

Solutions were prepared by adding the pure compound (as received) to purified (distilled and deionized) water (Millipore Milli-Q Plus) in a temperature-controlled cell. After dissolution of the compound, the electrodes were introduced, and the I^- signal was monitored until completion. For the spectrophotometric method, an aliquot of the solution was removed and placed in a temperature-controlled optical cell (10 cm path length). Starting concentrations of all species for these measurements were approximately 1×10^{-4} mol dm^{-3}. This concentration is below the saturation level of the compounds studied, but high enough to ensure an adequate increase in absorbance as the reaction progresses. To avoid loss of the compound to the gas phase, the cell was completely filled to eliminate any headspace. The water pH was slightly acidic (~pH 6) at the start of a test, but was not controlled or buffered and generally decreased to ~4 during the hydrolysis.

3.2 Partition coefficient determination

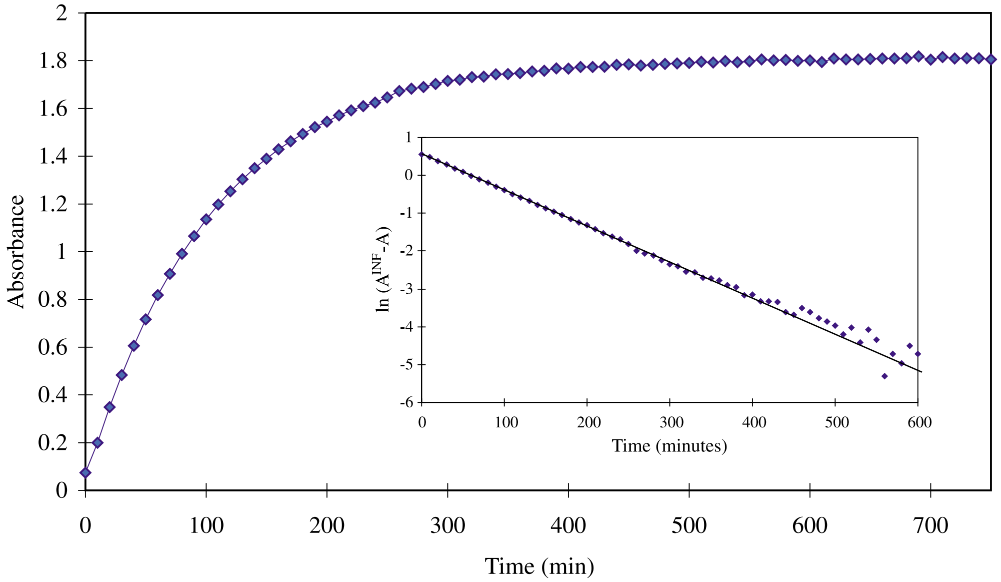
In this report, the partition coefficient (${}^{H}K$) is defined as the ratio of the aqueous phase concentration to the gas phase concentration at equilibrium.

$$[7] \qquad {}^{H}K = \frac{[\text{Compound(aq)}]_{eq}}{[\text{Compound(g)}]_{eq}}$$

Partition coefficients were determined in ~400 mL temperature-controlled cells at ambient pressure. Prior to being added to the temperature-controlled cell, 200 mL of purified water was purged with high purity air for 20–30 min. The vessel and water was conditioned at a given temperature for several hours before the pure compound, or an aliquot of a concentrated stock solution, was added to the aqueous phase of the vessel. A concentration of approximately 1×10^{-4} mol dm^{-3} was typically used for the partition coefficient measurement. For iodoethanol and iodoethanoic acid, a higher concentration (~1×10^{-3} mol dm^{-3}), which is still below saturation concentration, was used because of their low volatility.

Aqueous samples (400–1000 µL) were analyzed using a Waters high performance liquid chromatography system (LC-18 DB column, detection by UV at 254 nm). Gas samples (200–500 µL) were analyzed by gas chromatography (GC). The volatile species (iodomethane, iodoethane, and 2-iodobutane) were detected using a Varian GC system fitted with a photoionization detector, and an Altec polymethyl siloxane column (30 m, 0.53 mm i.d., 5 µm film thickness). The less volatile species required thinner phase capillary

Fig. 1. Growth of absorbance at 225 nm during the hydrolysis of iodoethane at 80°C. Inset shows the log plot of $A_{225\text{nm}}^{\text{INF}} - A_{225}$.



columns more suitable for polar compounds (which was on our HP Model 5972 GC–MS system). For iodophenol and iodoethanol, a J&W Scientific DB-1 column (30 m, 0.32 mm i.d., 3.0 µm film thickness) was used, and a HP-5 column (25 m, 0.32 mm i.d., 0.17 µm film thickness) was used for iodoacetic acid. Iodoethanoic acid, the least volatile of the compounds studied, required a solid phase micro extraction (SPME) technique (acrylate fibre) to concentrate material from the gas phase (17). This SPME fibre was calibrated with solutions of known concentration of iodoethanoic acid.

Equilibrium of the organic iodides between the gas and aqueous phase was generally reached within an hour, but sampling continued for several hours (every 30–60 min). Experiments were performed in duplicate.

4. Results

4.1 Hydrolysis rates

A typical absorbance growth curve at 225 nm observed during the hydrolysis of organic iodides is shown in Fig. 1.

The first-order rate constant for the hydrolysis of an organic compound was obtained from the growth curve of the absorbance at 225 nm as a function of time. The absorbance is related to the rate constant of the hydrolysis of the organic compound as follows.

Assuming that the rate of the hydrolysis reaction (rxn. [5]) has a first-order rate dependence[3] (more discussion in Section 5.1), the following expressions can be written:

$$[8] \qquad -\frac{d[\text{RI(aq)}]_t}{dt} = \frac{d[\text{I}^-]_t}{dt} = k \cdot [\text{RI(aq)}]_t$$

$$[9] \qquad [\text{RI(aq)}]_t = [\text{RI(aq)}]_0 \cdot e^{-kt}$$

$$[10] \qquad [\text{I}^-]_t = [\text{I}^-]_o + [\text{RI(aq)}]_o(1 - e^{-kt})$$

$$[11] \qquad [\text{ROH(aq)}]_t = [\text{ROH(aq)}]_o + [\text{RI(aq)}]_o(1 - e^{-kt})$$

where k is the rate constant for the hydrolysis reaction of organic iodide, $[\text{RI(aq)}]_t$, $[\text{I}^-]_t$, and $[\text{ROH(aq)}]_t$ are the concentrations of reactant, organic iodide, and products, iodide and alcohol, at time t, and $[\text{RI(aq)}]_o$ and $[\text{I}^-]_o$ are the initial concentrations of organic iodide and iodide.

The main contributor to the absorbance at 225 nm is I^-, but alcohols and organic iodides also absorb at this wavelength:

$$[12] \qquad A_{225\text{nm}}(t) = \varepsilon_{\text{I}^-}[\text{I}^-]_t + \varepsilon_{\text{ROH}}[\text{ROH(aq)}]_t + \varepsilon_{\text{RI}}[\text{RI(aq)}]_t$$

where $A_{225\text{nm}}$ is the observed absorbance at 225 nm, and ε_{I^-}, ε_{RI}, ε_{ROH} are the molar absorptivities of iodide, the organic iodide, and the corresponding alcohol, at 225 nm, respectively. Therefore, the observed absorbance as a function of time, $A_{225\text{nm}}(t)$ has the following relationship:

$$\begin{aligned}
[13a] \qquad A_{225\text{nm}}(t) &= \varepsilon_{\text{I}^-}([\text{I}^-]_o + [\text{RI(aq)}]_o(1 - e^{-kt})) \\
&+ \varepsilon_{\text{ROH}}([\text{ROH(aq)}]_o + [\text{RI(aq)}]_o(1 - e^{-kt})) \\
&+ \varepsilon_{\text{RI}}[\text{RI(aq)}]_o \cdot e^{-kt} = (\varepsilon_{\text{I}^-}[\text{I}^-]_o \\
&+ \varepsilon_{\text{ROH}}[\text{ROH(aq)}]_o + \varepsilon_{\text{RI}}[\text{RI(aq)}]_o) \\
&+ (\varepsilon_{\text{I}^-} + \varepsilon_{\text{ROH}} - \varepsilon_{\text{RI}})[\text{RI(aq)}]_o(1 - e^{-kt}) \\
&= A_{225\text{nm}}(t = 0) + (\varepsilon_{\text{I}^-} + \varepsilon\text{ROH} \\
&- \varepsilon_{\text{RI}})[\text{RI(aq)}]_o(1 - e^{-kt}) = A_{225\text{nm}}^{\text{INF}} \\
&- (\varepsilon_{\text{I}^-} + \varepsilon_{\text{ROH}} - \varepsilon_{\text{RI}})[\text{RI(aq)}]e^{-kt}
\end{aligned}$$

where $A_{225\text{nm}}(t = 0)$ is the absorbance at 225 nm at time zero (see eq. [12]) and $A_{225\text{nm}}^{\text{INF}}$ is the absorbance at 225 nm at time infinity (i.e., when the reaction is completed);

$$[13b] \qquad A_{225\text{nm}}^{\text{INF}} = A_{225\text{nm}}\ (t = \infty) = A_{225\text{nm}}\ (t = 0) + (\varepsilon_{\text{I}^-} + \varepsilon_{\text{ROH}} - \varepsilon_{\text{RI}})[\text{RI(aq)}]_o$$

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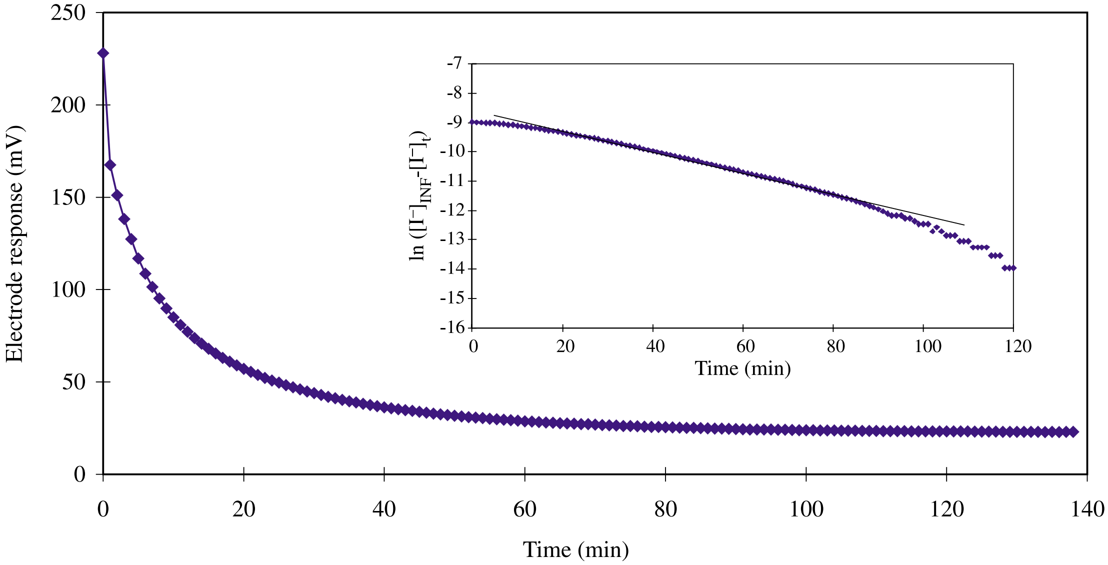
[3] The hydrolysis of organic iodides occurs via either an $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ mechanism (see section 5.1). For a given constant pH, both mechanisms yield a first-order dependent rate equation.

Fig. 2. Plot of electrode response during the hydrolysis of 2-iodobutane at 60°C. Inset shows the log plot of [I⁻].



Equation [13*a*] can be rewritten as:

$$[13c]\quad \ln A^{\mathrm{INF}}_{225\mathrm{nm}}\,(-A_{225\mathrm{nm}}(t)) = \ln((\varepsilon_{\mathrm{I}^-} + \varepsilon_{\mathrm{ROH}} - \varepsilon_{\mathrm{RI}})[\mathrm{RI(aq)}]_{\mathrm{o}}) - kt = \mathrm{const} - kt$$

The plot of ln $A^{\mathrm{INF}}_{225\mathrm{nm}}$ $(-\ A_{225\mathrm{nm}}(t))$ vs. time therefore provides the rate constant for hydrolysis of RI. The absorbance growth curve is replotted in the semi-log scale in the inset of Fig. 1 and shows first-order behaviour.

A sample electrode response observed of the hydrolysis of 2-iodobutane is shown in Fig. 2. The signal was first converted into I^- concentration according to the probe calibration. The $[I^-]_\infty - [I^-]_t$ is plotted on a log scale in the inset of Fig. 2, because the slope yields the rate constant.

$$[14]\quad \ln([I^-]_\infty - [I^-]_t) = \mathrm{const} - kt$$

Because the response is nonlinear, there is greater uncertainty at the beginning of the experiment. The uncertainty becomes larger again later when the electrode response is very small. This was considered when extracting a *pseudo*-first-order rate constant from the log plot, i.e., more weight was given to the data points in the middle of the test. As mentioned in Section 3.1, the iodide electrode method was used only for the hydrolysis of 2-iodobutane.

The hydrolysis of all the organic iodides studied in this work exhibited a first-order dependence on organic iodide concentration. Furthermore, the rate constant (k) for the organic iodide hydrolysis was, in general, observed to have a simple Arrhenius temperature dependence (Figs. 3–5), suggesting that the main hydrolysis mechanism did not change over the temperature range studied.

Repeat measurements agreed to within 10%, except for iodomethane and iodoethanoic acid. For these cases, the longer duration required for each measurement made reproducibility more difficult to achieve. The rate constants at 70°C (or at a specified temperature if 70°C data were not obtained) and the activation energies are summarized in Table 2. Also given in the table are the values of the preexponential factors that provide the best fits to the data over the studied temperature ranges. Individual data are discussed in more detail below.

Iodoalkanes

The hydrolysis rate for alkyl iodides was observed to increase from primary (iodomethane and iodoethane) to secondary (2-iodobutane) to tertiary (2-iodo-2-methylpropane) compounds. Because of the low rate, measurements for iodomethane were made only at higher temperatures. The rate constants obtained at 50 and 60°C have higher uncertainty because only a small portion of the organic iodide had hydrolysed over the test period. The reproducibility improved at 70°C, where the standard error was ~20%, based on the standard deviation of the measurements made at each temperature. The iodomethane data obtained in this work were compared to data available in the literature (Fig. 3), showing reasonable agreement with data taken from Laughton and Robertson (18), Moelwyn-Hughes (19), and Adachi et al. (20). Adachi et al. (20) presented formulas to generate both the S_N1 and the S_N2 rate constants at each temperature. The line in Fig. 3 attributed to Adachi et al. (20) was generated from the formula for the S_N1 rate constant.

The activation energy measured in the current work is (104 ± 10) kJ mol^{-1} and is slightly lower than the value (115 kJ mol^{-1}) reported by Adachi et al. (20). A fit to Moelwyn-Hughes' data provides an activation energy of 106 kJ mol^{-1}. The uncertainty quoted for the activation energies measured in the current work is the statistical standard error of the regression analysis.

The hydrolysis rate of iodoethane (a primary alkyl iodide) was only marginally faster than that of iodomethane at a given temperature (Fig. 4). An activation energy of (100 ± 6) kJ mol^{-1} was determined for the hydrolysis of iodoethane. For the determination of the activation energy, less emphasis was placed on the lower temperature data points due to the uncertainty in the measurements. Also shown in Fig. 4 is the value measured by Laughton and Robertson (18) at 99°C, which falls on the linear extrapolation of the Arrhenius dependence of our 60–90°C data.

Fig. 3. Arrhenius plot for the hydrolysis of iodomethane.

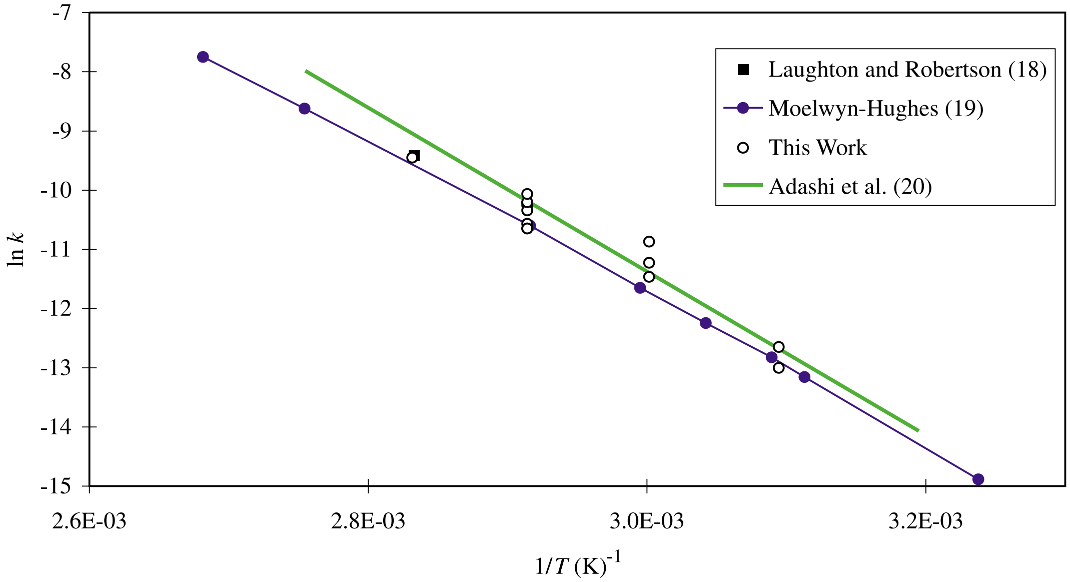
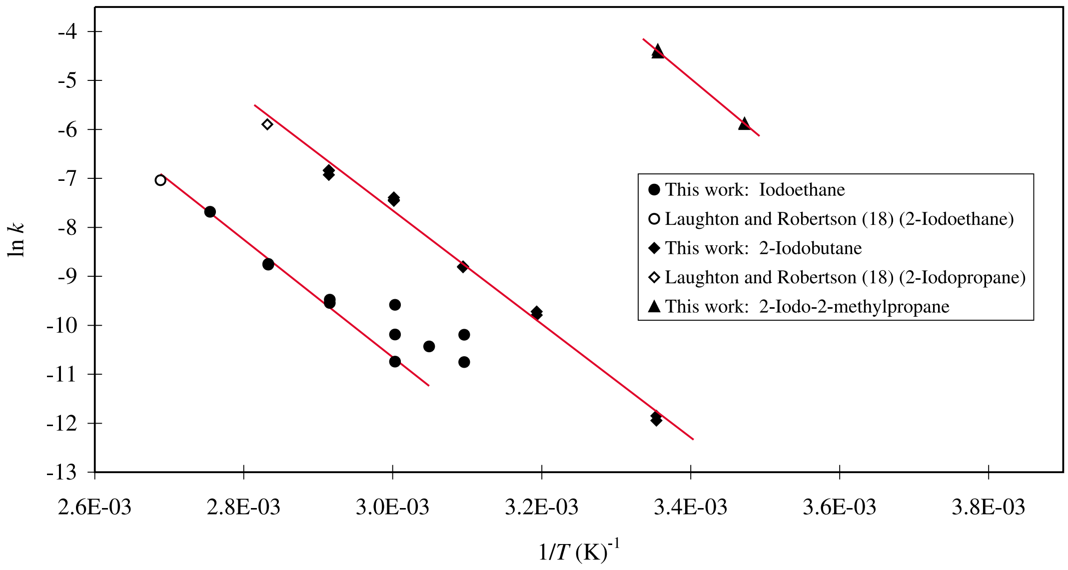


Fig. 4. Arrhenius plot for the hydrolysis of iodoethane, 2-iodobutane, and 2-iodo-2-methylpropane. Laughton and Robertson's (18) values for iodoethane and 2-iodopropane (another secondary iodide) are also included. Note that the "hydrolysis" of 2-iodo-2-methylpropane was performed in a 70% methanol:30% water solution.



The hydrolysis rates of the secondary alkyl iodide (2-iodobutane) were obtained using the iodide specific electrode method. The observed rates are in line with other data in the literature on hydrolysis of secondary iodides (Fig. 4). Extrapolating the 2-iodobutane results to 80°C yields a hydrolysis rate of about 3.3×10^{-3} s^{-1}, which is comparable to Laughton and Robertsons's (18) 2-iodopropane value of $(2.75 \pm 0.004) \times 10^{-3}$ s^{-1} at this temperature. An activation energy of (97 ± 5) kJ mol^{-1} was determined for 2-iodobutane.

The hydrolysis rate for the tertiary alkyl iodide (2-iodo-2-methylpropane) was very fast, and could not be measured in pure water using the chosen method. Instead, a lower limit for the hydrolysis rate for the compound was determined in a 30% water, 70% methanol solution at only two temperatures (15 and 25°C) (Fig. 4). This slowed the reaction down to the point where it could be measured ($t_{1/2}$ ~ 60 s), however, there may be a mixture of reactions occurring (i.e., the methanol may be reacting with the 2-iodo-2-methylpropane to form an ether). Therefore, the measurement is considered to be a lower limit for the hydrolysis reaction. An activation energy of ~106 kJ mol^{-1} was determined from the data assuming a simple Arrhenius dependence.

Organic iodides with functional groups

The hydrolysis rates for (iodomethyl)benzene (benzyl iodide) were measured using the spectrophotometric method. Difficulties encountered due to the low solubility of this compound were circumvented by decanting an aliquot of homogeneous solution from a dissolution vessel to avoid undissolved globules of (iodomethyl)benzene at the bottom of the reaction vessel.

Fig. 5. Arrhenius plot for the hydrolysis of (iodomethyl)benzene and iodoacetic acid.

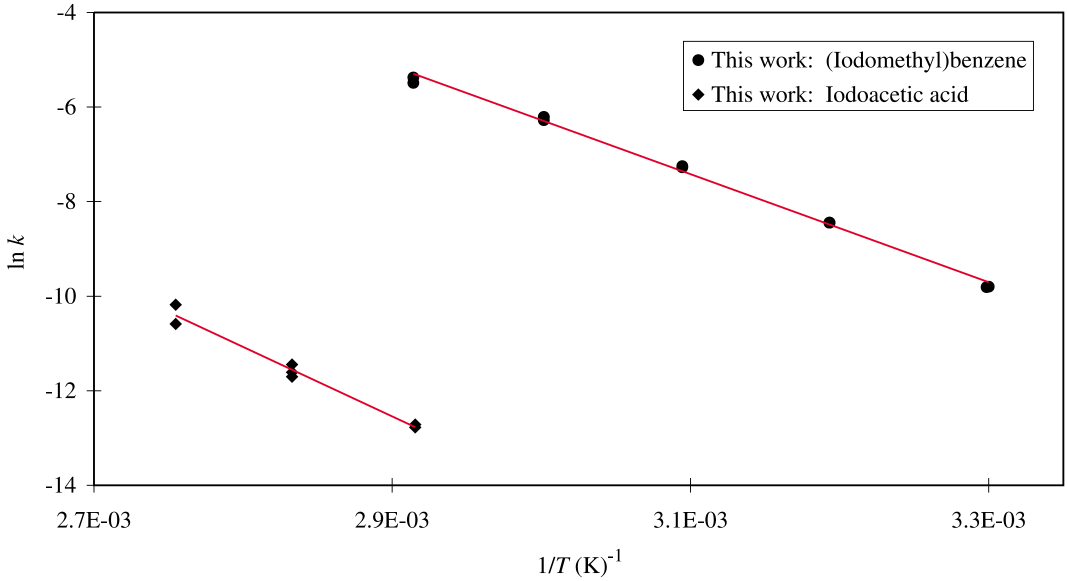


Table 2. Hydrolysis rates and temperature dependencies.

Compound	Hydrolysis rate at 70°C (s^{-1})[a]	Temperature dependence ($Ae^{-E_a/RT}$)	
		ln (A)[b]	E_a (kJ mol^{-1})[b]
Iodomethane	$(3.2 \pm 0.7) \times 10^{-5}$	26.0 ± 4.0	104 ± 10
Iodoethane	$(7.4 \pm 0.3) \times 10^{-5}$	25.4 ± 2.0	100 ± 6
2-Iodobutane	$(1.04 \pm 0.06) \times 10^{-3}$	27.1 ± 1.2	97 ± 5
Iodoethanoic acid	$(2.92 \pm 0.08) \times 10^{-6}$	33.6 ± 3.2	122 ± 10
(Iodomethyl)benzene	$(4.4 \pm 0.3) \times 10^{-3}$	27.1 ± 0.8	95 ± 5
Iodoethanol[c]	$(1.8 \pm 0.1) \times 10^{-5}$ (at 90°C)	Not determined	Not determined
2-Iodobenzenol	$<6 \times 10^{-8}$ (at 80°C)[d]	Not determined	Not determined
2-Iodo-2-methylpropane	$>1.2\times 10^{-2}$ (at 25°C)[e]	38.2 ± 0.9[f]	106 ± 2[f]

[a] Uncertainty given is the statistical standard error in the duplicate measurements at a given temperature. The error given for the rate is the standard deviation among the measured values.

[b] Uncertainty is the statistical standard error of the Arrhenius fit to the data.

[c] Only two measurements were made, both at 90°C.

[d] Estimated upper limit.

[e] Lower limit estimated in a 70% methanol/30% water solution. It is not known if methanol is reacting with the 2-iodo-2-methylpropane as well.

[f] Estimate based on data from a 70% methanol/30% water solution.

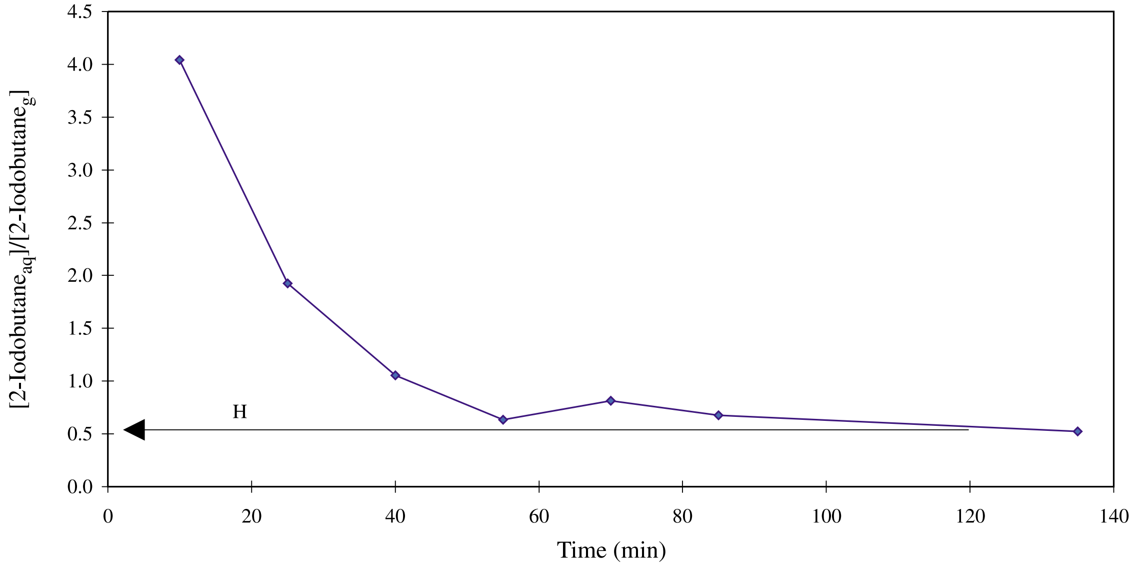
The Arrhenius plot (Fig. 5) appears linear over the range of temperatures measured (30–70°C), and extrapolation to the entire aqueous range (0–100°C, at a total pressure of 1 bar) should be acceptable. The rates of this reaction can be compared to those of other benzyl halides measured by Laughton and Robertson (18) (2.7×10^{-4} s^{-1} at 30°C for (bromomethyl)benzene and 5.8×10^{-4} s^{-1} at 60°C for (chloromethyl)benzene). The rate of (iodomethyl)benzene hydrolysis seems to fall in between the rates of (bromomethyl)benzene and (chloromethyl)benzene hydrolysis, a trend that has been noted in the past for alkyl halides (18, 19). An activation energy of 95 ± 5 kJ mol^{-1} was extracted from the data.

The hydrolysis rate of iodoethanoic acid was slower than that of iodoethane (and therefore only high temperature measurements were made), even though the basic carbon chain is the same. Iodoethanoic acid has a pK_a of 3.12 (21); therefore, most of it would have been dissociated at the starting pH of the solution (measured at approximately 4.5). One can speculate that perhaps the hydrolysis occurs with primarily the neutral form, the concentration of which, under these conditions, is effectively reduced. The larger field and steric effects of the carboxylic acid group in iodothanoic acid, compared to the effects of alkyl group in iodoethane, may also contribute to the slower hydrolysis rate (22). An activation energy of 122 ± 5 kJ mol^{-1} was extracted from the Arrhenius plot.

Iodoethanol has a very slow hydrolysis rate. Due to the length of time required for the measurements, the rate constant was measured only at 90°C, and was found to be $(1.8 \pm 0.1) \times 10^{-5}$ s^{-1} (average of two values).

The rate of hydrolysis for 2-iodobenzenol (2-iodophenol) was too slow to measure directly. The rate was estimated to be less than 6×10^{-8} s^{-1}, based upon the minor increase in absorbance observed after 85 h at 80°C.

Fig. 6. Ratio of the aqueous to gas phase concentration of 2-iodobutane as a function of time after the pure compound is introduced into the aqueous phase of the vessel (60°C).



4.2 Partition coefficients

Henry's Law states that at equilibrium, the solubility of a gas is proportional to the partial pressure of the gas (P_{Compound}) above the liquid phase:[4]

$$[15] \quad \text{Henry's Constant} = \left(\frac{[\text{Compound(aq)}]}{P_{\text{Compound}}}\right)_{\text{eq}}$$

There are many units available to describe this ratio because there are many different units of pressure and concentration (e.g., mol dm^{-3} atm^{-1}). In this document, we use the term "partition coefficient" and the symbol "${}^{\mathrm{H}}K$" to signify a unitless form of Henry's Law constants as it is a more commonly adopted definition in the nuclear industry (see eq. [7]).

Henry's Law constants depend upon temperature, and are independent of the volume of gas or volume of liquid phase. The partition coefficients of the organic iodides were observed to follow a simple exponential temperature dependence over the studied temperature range:

$$[16] \quad \ln {}^{\mathrm{H}}K^{T} = \ln {}^{\mathrm{H}}K^{298} + \left(\frac{-\Delta_r H^o}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right)$$

where T is absolute temperature, R is the gas constant, $\Delta_r H°$ is the enthalpy of reaction (i.e., gas–aqueous phase partitioning) and ${}^{\mathrm{H}}K^{T}$ and ${}^{\mathrm{H}}K^{298}$ are the partition coefficients of a given compound at temperature T and 25°C (298 K).[5]

In this work, the aqueous and gas samples were analyzed simultaneously as a function of time until the system reached equilibrium between the aqueous and gas phases. The equilibrium was generally reached within an hour, but sampling continued for several hours (every 30–60 min). An example of the ratio of the aqueous phase concentration to the gas phase concentration observed as a function of time is shown in Fig. 6. Shown in the figure are data for 2-iodobutane at 60°C. The limiting value provides the partition coefficient (${}^{\mathrm{H}}K$).

The results are summarized in Tables 3 and 4 along with the literature values of similar organic iodides. The examples of the scatter in the data for the partition coefficient and its temperature dependence are presented in Figs. 7 and 8 for iodomethane and iodoethanol. Individual data are discussed below.

Iodoalkanes

The partition coefficient of iodomethane determined in this study showed an exponential relationship of $\ln {}^{\mathrm{H}}K = (3430 \pm 60)/T - (9.9 \pm 0.2)$ (Fig. 7). Our results agree with the partition coefficient measured by Hunter-Smith et al.

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[4] This law holds for solutions dilute enough that the environment of the solute remains constant. Mackay and Shiu (23) suggest a mol fraction of 0.01 as an upper limit.

[5] The partition coefficient is an equilibrium constant, and has the following relationship at a given temperature:

$$\Delta_r G° = -RT \ln ({}^{\mathrm{H}}K/RT) = \Delta_r H^{\circ}_{T} - T\Delta_r S°$$

$$\text{or} \quad \ln ({}^{\mathrm{H}}K) - \ln (RT) = -(\Delta_r H^{\circ}_{T}/RT) + \Delta_r S°/R$$

where ${}^{\mathrm{H}}K$ is the Henry's constant as defined in eq. [15]. The use of eq. [16] to determine the exponential temperature dependence of the partition coefficient thus implies that the $\Delta_r H°$ value reported in this document is the average enthalpy of the gas–liquid partitioning over a temperature range of the aqueous phase. Over the studied temperature range, the enthalpy of the partitioning of the organic iodides appears to be nearly temperature-independent. The use of eq. [16] also implies that the second term of the left hand side of the above thermodynamic relationship (ln (RT)) is ignored in obtaining the slope (the contribution of the term to the slope is very small). Thus, the $\Delta_r H°$ value reported here is the enthalpy of reaction to a first-order approximation.

Table 3. Effect of iodine atoms on partition coefficients.

Compound	^{H}K (25°C)	Reference	Iodine-substituted compound	^{H}K (25°C)	Reference	Rel. ratio
Methane	0.04	27	Iodomethane	4.82 ± 0.01	This work	120
			Diiodomethane	56	23	1400
			Triiodomethane	88	28	2200
Ethane	0.05	27	Iodoethane	2.84 ± 0.01	This work	57
Propane	0.04	27	1-Iodopropane	2.6	23	65
			2-Iodopropane	2.2	23	55
Butane	0.03	27	1-Iodobutane	1.5	23	50
			2-Iodobutane	2.1 ± 0.3	This work	70
Benzene	4.5	27	Iodobenzene	19	27	4
Chloromethane	2.6	27	Chloroiodomethane	22	23	8
Ethanol	4900	23	Iodoethanol	73 000 ± 3000	This work	15
Ethanoic acid	127 000	23	Iodoethanoic acid	490 000 ± 90 000	This work	4

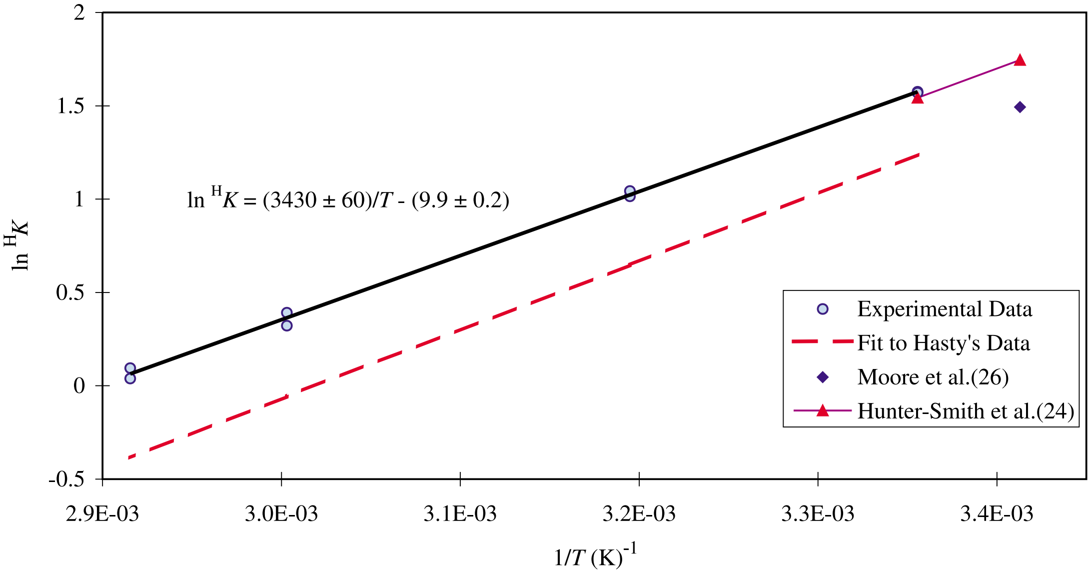
Note: The errors listed are the statistical standard error.

Table 4. The temperature dependence of partition coefficients of compounds with and without iodine atoms.

Compound	$-\Delta_r H°/R^a$ (K)	Reference	Iodine-substituted compound	$-\Delta_r H°/R^a$ (K)	Reference
Methane	1800	23	Iodomethane	3430 ± 60	This work
			Diiodomethane	5000	26
Chloromethane	3000	26	Chloroiodomethane	4300	26
Ethane	2300	23	Iodoethane	3800 ± 120	This work
Butane	3100	23	2-Iodobutane	3400 ± 400	This work
Ethanol	6600	23	Iodoethanol	7900 ± 600	This work
Ethanoic acid	6400	23	Iodoethanoic acid	11 500 ± 800	This work

Note: The errors listed are the statistical standard error.
[a]See footnote 5.

Fig. 7. Temperature dependence of the partition coefficient of iodomethane.



(24), and to within 20–60% of those obtained by Hasty (25), and Moore et al. (26). The partition coefficients of Iodoethane and 2-iodobutane and their temperature dependences are very similar to those of iodomethane (Tables 3 and 4).

Organic iodides with functional groups

For the remaining compounds, the partition coefficients of only iodoethanol and iodoethanoic acid were obtained.[6] These compounds are highly soluble in water and have very high partition coefficients and steep temperature

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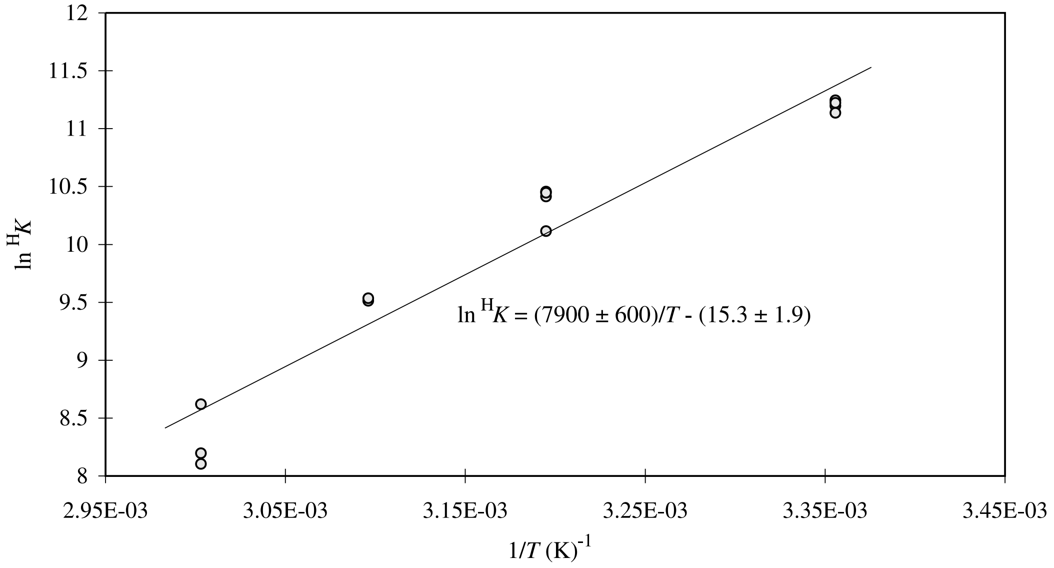
[6] The partition coefficients of (iodomethyl)bezene and 2-iodo-2-methylpropane could not be determined because they hydrolysed too quickly to obtain any meaningful results.

Table 5. Literature hydrolysis rates.

Compound	Temperature (°C)	Rate constant (s^{-1})	Reference
Iodomethane	60	8.72×10^{-6}	19
Iodomethane	60	2.3×10^{-5}	20
Iodomethane	70	2.49×10^{-5}	19
Iodomethane	80	2.34×10^{-4}	20
Iodomethane	80	8.19×10^{-5}	18
Iodomethane	90	1.8×10^{-4}	19
Iodoethane	99	8.78×10^{-4}	18
2-Iodopropane	80	2.75×10^{-3}	18
1-Iodopropane	100	5.49×10^{-4}	18
1-Iodo-2-methylpropane	100	3.55×10^{-4}	18

Fig. 8. Temperature dependence of the partition coefficient of iodoethanol.



dependences (Tables 3 and 4, see also Fig. 8). Because of the high partition coefficients, a higher aqueous concentration (~1×10^{-3} mol dm^{-3}) was used for these compounds to ensure a detectable amount in the gas phase. Furthermore, for iodoethanoic acid, a microextraction technique was used for the gas phase detection, in which small amount of iodoethanoic acid was adsorbed and concentrated onto a micro-extraction fibre before injection into the GC.

5. Discussion

5.1 Hydrolysis rates

Hydrolysis of halogenated aliphatic compounds (rxn. [5]) occurs via well-known nucleophilic substitution mechanisms (S_N1 and S_N2). Because the relative contribution of these two mechanisms to the overall hydrolysis of organic iodides impacts on the dependence of its rate on the OH^- concentration, the nucleophilic substitute mechanisms are reviewed briefly below, prior to the discussion on the hydrolysis rate of organic iodides.

The S_N2 hydrolysis reaction of iodo-compounds is a second-order process, with a rate dependent upon the concentration of both OH^- and the organic iodide. Because of the dependence on $[OH^-]$, the hydrolysis rate of organic iodides would depend strongly on pH. Because the S_N2 mechanism involves the hydroxide ion approaching the reactive carbon, steric hindrance affects the rate. Therefore, the relative S_N2 hydrolysis rate at a given pH and temperature, is as follows (21, 29):

methyl > primary > benzylic > secondary > tertiary

The S_N1 reaction rate depends only on the concentration of iodo-alkane because the rate-determining step is the unimolecular dissociation of the carbon—halogen bond. Thus, for S_N1, the hydrolysis rate depends on the stability (and therefore, the structure) of the intermediate carbocation, and the relative S_N1 rates are (21, 29):

tertiary > secondary, benzylic > primary, methyl

The structure of the iodo-compound and the OH^- concentration governs which one of the two nucleophilic substitution mechanisms is dominant. The primary alkyl-iodides should be the most sensitive to pH, as they can hydrolyse faster than other iodo-compounds via the S_N2 reaction, where the nucleophile is OH^-. Thus, if there were any significant pH dependence of hydrolysis rate, it would be most pronounced for iodomethane. Adachi et al. (20) have measured both the S_N1 and S_N2 rates of iodomethane hydrolysis separately, over a temperature range of 25–65°C. Their measurements show that, at a given temperature, the S_N2 contribution to the overall hydrolysis of iodomethane is negligible at pH 6, and does not become significant until about pH 11. Therefore, the S_N2 portion of the reaction can be ignored for the pH range studied in this work. Furthermore, since methyl iodide represents the structure which undergoes S_N2 hydrolysis the fastest, it follows that the S_N2 portion of the hydrolysis rates of all other iodinated compounds can be ignored as well, for the pH range used in this work, and for the pH range (pH 4–10) expected in containment.

Table 5 lists the hydrolysis rates of various alkyl iodides reported by other groups (18–20). (The hydrolysis rates measured in the current study are summarized in Table 2). A hydrolysis rate of $(3.2 \pm 0.7) \times 10^{-5}\ \mathrm{s}^{-1}$ at 70°C and an activation energy of $(104 \pm 10)\ \mathrm{kJ\ mol}^{-1}$ obtained for iodomethane in this study are in good agreement with the values observed by Molewyn-Hughes (19): a hydrolysis rate of $2.49 \times 10^{-5}\ \mathrm{s}^{-1}$ at 70°C and an activation energy of $106\ \mathrm{kJ\ mol}^{-1}$. Adachi et al. (20) obtained an activation energy of $113\ \mathrm{kJ\ mol}^{-1}$ for the S_N1 portion of the reaction, and also provided an expression for the temperature dependence for the S_N2 contribution.

Since the main mechanism for the hydrolysis of organic iodides under the experimental conditions (and also expected under accident conditions) is S_N1, the hydrolysis can be expressed as a simple first-order process. The first-order rate constant (k) for the hydrolysis of organic iodides (given in Tables 2 and 5) varies widely at a given temperature. The observed trend is in good agreement with the relative rates expected for S_N1 reactions previously discussed: slow for primary alkyl iodides (e.g., $(3.2 \pm 0.7) \times 10^{-5}\ \mathrm{s}^{-1}$ at 70°C for iodomethane) and aromatic iodides (e.g., less than $6 \times 10^{-8}\ \mathrm{s}^{-1}$ for 2-iodobenzenol) and faster for benzylic and secondary alkyl iodides (e.g., $(4.4 \pm 0.3) \times 10^{-3}\ \mathrm{s}^{-1}$ for (iodomethyl)benzene and $(1.04 \pm 0.05) \times 10^{-3}\ \mathrm{s}^{-1}$ for 2-iodobutane) and fastest for tertiary alkyl iodides (e.g., very fast even at 25°C for 2-iodo-2-methylpropane). As could be predicted by its nucleophilic substitution mechanism, the most important factor affecting hydrolysis rate is the position of the iodine atom on the carbon structure, rather than the number of carbons in the molecule. For example, 1-iodobutane would be expected to have a hydrolysis rate comparable to that of iodoethane (another primary iodide).

Functional groups adjacent to the iodide atom appear to modify the rates slightly as well (e.g., the hydrolysis rates of iodoethanoic acid and iodoethanol are lower than that of iodoethane). More data would be required to fully assess the effect of functional groups.

The rate constants of the organic iodides studied were observed to have a simple Arrhenius temperature dependence, indicating that for a given compound, the main hydrolysis mechanism (i.e., S_N1 for all the compounds studied) did not change over the temperature range studied. The observed trend for the activation energy also follows that expected from the S_N1 mechanism, lower for (iodomethyl)benzene and 2-iodobutane than for primary alkyl iodides or iodoethanoic acid.

Table 6. Selected partition coefficients (25°C) for various classes of compounds.

Compound class	Examples	^{H}K (approx.)[a]
Alkanes	Hexane	0.02
Alcohols	Methanol	5300
	Ethanol	4900
	Butanol	2900
	Hexanol	1500
	Phenylmethanol	220 000
Diols	1,2-Ethanediol	9.8×10^7
Aldehydes	Formaldehyde	73 000
	Acetaldehyde	370
	Hexanal	120
Ketones	Acetone	730
	Methyl ethyl ketone	500
	Methyl isobutyl ketone	54
Carboxylic acids	Ethanoic acid	122 000
	Phenylmethanolic acid	580 000
	Hexanoic acid	29 000
Aromatic	Benzene	4.5
	Toluene	4.1
	1,4-Dimethylbenzene	3.2
	Ethyl benzene	3.2
	Styrene	9
Phenolic	Benzenol	39 000
	4-Methylbenzenol	15 000
Multifunctional	Phenylmethanol	220 000
	Hydroxyethanol	1 000 000
	Hydroxypropanoic acid	1.7×10^9
	Propanonal	780 000

[a] Values taken from refs. 23 and 27.

5.2 Partition coefficients

Partition coefficients reported in the literature, along with our data, are listed in Tables 3 and 6. Also shown in these tables are the partition coefficients of non-iodine substituted organic compounds. Comparison of the partition coefficients of these organic iodides with their non-iodine-substituted counterparts provides a reasonable approach to estimate the partition coefficients of other organic iodides. The partition coefficients of organic compounds at 25°C are reviewed first, followed by their temperature dependencies.

Table 3 compares the partition coefficients at 25°C of the few measured organic iodides to those of their non-iodine-substituted counterpart. An examination of Table 3 shows that substituting an iodine atom into a molecule makes the compound less volatile, but the impact of the change decreases as the partition coefficient increases.

Studies on Henry's Law constants have found relationships between the partition coefficient and structural components of a molecule, such as bonds and functional groups (30–33). In general, hydrophilic components such as halogen, oxygen, nitrogen, and sulphur containing functional groups increase the partition coefficient, whereas hydrophobic components such as long chains of carbon—carbon bonds and carbon—hydrogen bonds, decrease the partition coefficient. Some of these trends are apparent by examining the values listed in Tables 3 and 6. Several methods of estimating partition coefficients by empirically correlating partition coefficients with structural parameters have been devised (30–33). These methods provide ways to predict Henry's Law constants for molecules with different functional groups to within a factor of two or three, based upon

Table 7. Range of temperature dependencies of ^{H}K for various classes of organic compounds.

Compound Class	Range of $-\Delta_r H°/R^a$ (K)	Examples	$-\Delta_r H°/R^a$ (K)
Alkanes	1500–8000	Methane	1800
		Butane	3100
Alcohols	5000–8000	Methanol	5400
		Butanol	7300
		2-Propanol	7500
Aldehydes	4000–9000	Methanal	7000
		Ethanal	5000
		Hexanal	6500
Ketones	4000–10 000	Propanone	5000
		2-Butanone	5500
		3-Pentanone	9200
Carboxylic acids	5700–11 000	Ethanoic acid	6400
		Phenylmethanoic acid	6500
		Hexanoic acid	6300
Aromatic (one ring)	3000–5000	Benzene	4000
		Methylbenzene	4000
		1,4-Dimethylbenzene	5000
Phenolic	7000–8000	Benzenol	7000
		4-Methylbenzenol	7300
Multifunctional	—	Hydroxyethanol	4600
		Propanonal	7500

[a] Ranges and approximate values taken from ref. 27.

sets of compounds for which the constant has been experimentally determined. These structure-based calculation methods predict the trend observed in Table 3 that the substitution of an iodine atom for a hydrogen atom within a molecule generally increases the partition coefficient. This increase ranges from two orders of magnitude for low solubility alkane organic compounds (i.e., methane to butane in Table 3), to a factor of 5–10 for highly soluble organic compounds containing a carbonyl, alcohol, or carboxylic acid group.

Table 6 lists the partition coefficients of non-iodinated compounds, from which the partition coefficients of the counterpart organic iodides can be estimated. In general, the partition coefficient increases with the number of oxygen atoms, and decreases with length of the carbon chain. Not all functional groups containing one oxygen atom are equal though; for example, alcohols have much higher partition coefficients than ketones.

The temperature dependences for the partition coefficients of organic iodides reported in the literature and from this work are compared with the temperature dependence of corresponding non-iodine-substituted (parent) organic compounds in Tables 4 and 7.

The value of $-\Delta_r H°/R$ of an organic iodide is consistently higher than that of the corresponding non-iodine-substituted organic compound for the small number of comparisons available (Table 4). However, the increase is small enough that the temperature dependencies of the partition coefficient of an organic iodide may be approximated from that of non-iodine-substituted counterpart. Table 7 lists the range of $-\Delta_r H°/R$ for various classes of organic compounds. The value of $-\Delta_r H°/R$ ranges from about 500–10 000 K. Organic iodides and corresponding non-iodine-substituted organic compounds that are more volatile than I_2 at 25°C (i.e., alkane and aromatic compounds), have $-\Delta_r H°/R$, of the order of 3400 K, whereas the other more soluble compounds have a $-\Delta_r H°/R$ of the order of 6500 K. Note that the partition coefficient of I_2 has a temperature dependence ($-\Delta_r H°/R$) of ~4000 K (34–36).

The pH is not likely to affect the partitioning of a compound, unless the solubility of a compound is affected, which is not expected to occur at the pH range expected in containment (pH < 11). However, for the compounds that have p*K*a values within the pH range being considered, the distribution between the acid and base forms must be considered.

5.3 Proposed grouping of organic iodides for reactor safety analysis applications

The wide range of organic iodides expected to be formed in containment following an accident presents several problems for models of iodine behaviour. The precise nature of the important organic iodides to be modelled cannot be predicted because of the number of different sources of organic material within containment, and the variety of organic species that may be derived from these sources. Detailed physical modelling of all of the possible organic species would be computationally intensive and fraught with uncertainty because precise rate information is lacking for many of the potential species. The review of the partition coefficients and hydrolysis rates provides a basis for reasonable and defensible grouping of organic iodide species, and the assignment of common rate constants. This would greatly simplify the challenge facing those who model iodine behaviour. The suggested grouping is presented below.

Recommended hydrolysis rates

If the division of organic iodides based on hydrolysis rates is required, it is recommended that the division be done on the basis of molecular structure because the hydrolysis rates of organic iodides are sensitive to the structure. Based on the hydrolysis rates listed in Tables 2 and 8, it is proposed that organic iodides be divided into two groups, primary alkyl iodides (PRI) and nonprimary organic iodides (NRI). The NRI group would include secondary, tertiary, and benzylic iodides, as well as any other carbon structure that would enhance hydrolysis rate.

The hydrolysis rates of primary alkyl iodides range from (2.92 ± 0.08) × 10^{-6} s^{-1} (iodoethanoic acid) to (7.4 ± 0.3) × 10^{-5} s^{-1} (iodoethane) at 70°C. Iodomethane appears to adequately represent the average behaviour of the primary alkyl group. After conversion to 25°C (using the activation energy measured in this work), the iodomethane values can be used to represent the primary alkyl iodides:

$$[17] \quad \ln k_{\mathrm{PRI}} = \ln k_{\mathrm{PRI}}^{298} + \frac{\Delta E_{\mathrm{a}}}{8.3145} \cdot \left(\frac{1}{298} - \frac{1}{T} \right)$$

where k_{PRI}^{298} = (1.3 ± 0.9) × 10^{-7} s^{-1}) and ΔE_a = 104 ± 10 kJ mol.

For the second group, the hydrolysis rate constants are larger than 1 × 10^{-4} s^{-1} at 70°C. For this group, 2-iodobutane is recommended to represent the average of the NRI organic iodides (after conversion to 25°C):

$$[18] \quad \ln k_{\mathrm{NRI}} = \ln k_{\mathrm{NRI}}^{298} + \frac{\Delta E_{\mathrm{a}}}{8.3145} \cdot \left(\frac{1}{298} - \frac{1}{T} \right)$$

where k_{NRI}^{298} = (7.7 ± 0.3) × 10^{-6} s^{-1}) and ΔE_a = 97 ± 5 kJ mol.

Recommended partition coefficients

Examination of Tables 3 to 7 reveals that the range of volatility of organic iodides can be enormous. However, under accident conditions, organic iodides would be formed from the reaction between organic radicals and molecular iodine (rxn. [3]). The fraction of molecular iodine converted to organic iodides is nearly independent of the type of organic impurities present in the containment sump. Hence, the most logical organization of organic iodides for modelling the volatility of organic iodides in containment following an accident is based on their partition coefficient with respect to that of molecular iodine, i.e., whether the compound is more or less volatile than molecular iodine. The partition coefficient of iodine (~79 at 25°C) (27, 34–36) is such that the division essentially corresponds to whether the compound contains oxygen or not. Except in rare cases, the presence of a single oxygen atom within a molecule raises the partition coefficient at a given temperature to above 100, whereas multiple oxygen atoms within a molecule generally raise the partition coefficient to well above 1000. Thus, the proposed strategy for managing the wide range of partition coefficients in containment under accident conditions is to divide organic iodides into two groups, which are based on their volatility relative to the volatility of I_2: (*i*) "high" volatility organic iodides (HVRI) such as alkyl iodides (e.g., methyl-, ethyl-, and butyl-iodides) and aromatic iodides (e.g., iodobezene); and (*ii*) "low" volatility organic iodides (LVRI) containing oxygen such as alcohol and acid (e.g., iodoethanol and iodoethanoic acid).

Since iodomethane exhibits the average behaviour of HVRI, the partition coefficient of iodomethane and its temperature dependence are recommended to represent the HVRI compounds:

$$[19] \quad \ln {}^{\mathrm{H}}K_{\mathrm{HVRI}} = \ln {}^{\mathrm{H}}K_{\mathrm{HVRI}}^{298} + \left((3430 \pm 60) \cdot \left(\frac{1}{T} - \frac{1}{298} \right) \right)$$

The LVRI compounds encompass a much broader range of compounds containing oxygen. A partition coefficient of (1000 ± 250), which is a conservatively averaged (i.e., a low value that provides a conservatively large gas phase concentration) value of alcohols, aldehydes, ketones, and acids from Table 6, is recommended to represent the partition coefficient of LVRI at 25°C. The temperature dependence of the partition coefficients of the LVRI compounds is also somewhat steeper than those of the HVRI compounds, with $-\Delta H/R$ generally ranging from 5000 to 7500 K. An intermediate value of (6500 ± 1000) K for $-\Delta H/R$ is therefore recommended to represent the temperature dependence of LVRI:

$$[20] \quad \ln {}^{\mathrm{H}}K_{\mathrm{LVRI}} = \ln {}^{\mathrm{H}}K_{\mathrm{LVRI}}^{298} + \left((6500 \pm 1000) \cdot \left(\frac{1}{T} - \frac{1}{298} \right) \right)$$

where ${}^{\mathrm{H}}K_{\mathrm{LVRI}}^{298}$ = (1000 ± 250).

The proposed organization and the assignment of the average partition coefficients should be evaluated with the proposed strategies for handling the other aspects of organic reactions. For example, the overall rate of organic iodide formation (via rxns. [1]–[3]) and the relative ratio of HVRI and LVRI formation are also crucial in determining organic iodide volatility in containment. The organization should be also consistent with the organic iodide decomposition processes, such as hydrolysis and radiolysis.

Conclusions

Experiments have been performed to obtain the partition coefficients and hydrolysis rates of various organic iodides. These data, and data accumulated in the literature, have been reviewed to provide guidelines for appropriate organization of organic iodides for the purpose of modelling iodine behaviour under postulated nuclear reactor accident conditions.

If the grouping of organic iodides based on hydrolysis rates is required, it could be done on the basis of molecular structure because the hydrolysis rates of organic iodides are sensitive to the structure. Thus, organic iodides could be divided into two groups, primary alkyl iodides (PRI) and nonprimary organic iodides (NRI). The NRI group would include secondary, tertiary, and benzylic iodides, as well as any other carbon structure that would enhance hydrolysis rate.

Based on the partition coefficients, organic iodides could be divided into two groups based upon their volatility relative to molecular iodine: (*i*) HVRI (high volatility organic iodides), which is comprised of alkyl iodides having a partition coefficient smaller than I_2; and (*ii*) LVRI (low volatility organic iodides), which is comprised of compounds generally containing at least one oxygen atom, and having a partition coefficient higher than that of I_2.

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